AD-A182 952   SURFACE ENHANCED RAMAN SCATTERING FROM OH- ADSORBED ON   1/1
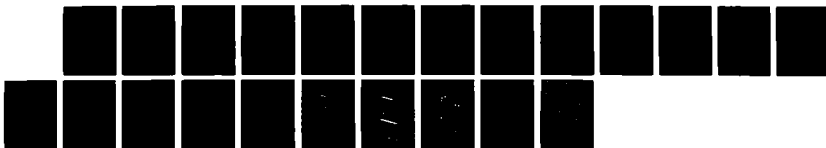   A AG ELECTRODE IN DILUTE MG+2 ELECTROLYTES(U) AMHERST
              COLL MA DEPT OF CHEMISTRY P B DORAIN 27 JUL 87 TR-14
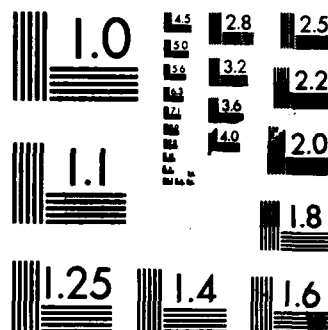UNCLASSIFIED N00014-85-K-01050   F/G 7/4   NL

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

⑫

AD-A182 952

OFFICE OF NAVAL RESEARCH

Contract No. N00014-85-K-01050

TECHNICAL REPORT NO. 4

Surface Enhanced Raman Scattering from OH$^-$ Adsorbed on a

Ag Electrode in Dilute Mg^{+2} Electrolytes

by

Paul B. Dorain

Amherst College
Amherst,Massachusetts 01002

DTIC
ELECTE
AUG 0 3 1987
S
E
D

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b RESTRICTIVE MARKINGS
UNCLASSIFIED	NONE

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for Public Release; Distribution Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
4	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Amherst College		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Chemistry Department Amherst, MA 01002	800 North Quincy Street Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		N00014-85-K-01050

8c. ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS			
800 North Quincy Street Arlington, VA 22217	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
(U) Surface Enhanced Raman Scattering from OH⁻ Adsorbed on a Ag Electrode in Dilute Mg^{+2} Electrolytes

12 PERSONAL AUTHOR(S)
Paul B. Dorain

13a. TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical Report	FROM _____ TO _____	1987 July 27	21

16. SUPPLEMENTARY NOTATION

Submitted for publication in J.Phys.Chem.

17	COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Surface Enhanced Raman Scattering (SERS), adsorbed, OH⁻, adsorbed Mg^{+2}, hydroxides, magnesium ions
	silver		

19. ABSTRACT (Continue on reverse if necessary and identify by block number) .01 .001

Surface enhanced Raman scattering (SERS) has been used to probe the adsorption of OH^{-} on a Ag electrode immersed in 10^{-2} to 10^{-3}M $MgCl_2$ containing micromolar quantities of either $KMnO_4$ or dissolved Cl_2. Strong spectra due to adsorbed OH⁻, nearly identical to those obtained previously in ≥ 1M $MgCl_2$ solutions, were obtained only if the oxidizing agent was present. Besides the O-H stretching modes near 3600 cm⁻¹, the low frequency modes due to the metal oxygen stretch are observed. A model is proposed in which adsorbed Mg^{+2} provides positive surface charge densities which are sites for adsorbing OH⁻. Three distinct adsorption sites are predicted which is in accord with the observation of three O-H species during H_2 production. These results, together with those previously obtained for alkali halides, indicate that corrosion processes in dilute aqueous media proceed by pathways dependent on the concentration and composition of dissolved salts which strongly affect the surface structure of water and its derivatives (keywords) > or =

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	UNCLASSIFIED

22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
Paul B. Dorain	(413) 542-2148	

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted. All other editions are obsolete

SURFACE ENHANCED RAMAN SCATTERING from OH⁻

ADSORBED on a Ag ELECTRODE in DILUTE Mg^{+2} ELECTROLYTES

Paul B. Dorain

Chemistry Department,

Amherst College,

Amherst, MA 01002

ABSTRACT

Surface enhanced Raman scattering (SERS) has been used to probe the adsorption of OH^- on a Ag electrode immersed in 10^{-2} to 10^{-3}M $MgCl_2$ containing micromolar quantities of either $KMnO_4$ or dissolved Cl_2. Strong spectra due to adsorbed OH^-, nearly identical to those obtained previously in $\geq$1M $MgCl_2$ solutions, were obtained only if the oxidizing agent was present. Besides the $O-H$ stretching modes near 3600 cm^{-1}, the low frequency modes due to the metal oxygen stretch are observed. A model is proposed in which adsorbed Mg^{+2} provides positive surface charge densities which are sites for adsorbing OH^-. Three distinct adsorption sites are predicted which is in accord with the observation of three $O-H$ species during H_2 production. These results, together with those previously obtained for alkali halides, indicate that corrosion processes in dilute aqueous media proceed by pathways dependent on the concentration and composition of dissolved salts which strongly affect the surface structure of water and its derivatives.

INTRODUCTION

The structure of water at or near the surface of a metal on which there may be other adsorbed molecular species is important in understanding the chemistry of corrosion, electrolysis, wetting, and many catalytic oxidation processes [1-4]. Until the advent of surface enhanced Raman scattering (SERS) it was difficult to probe *insitu* the vibrational properties of interfacial water and its chemical derivatives with spectroscopic techniques because of the low surface concentration. SERS, being sensitive to less than monolayer coverage of adsorbates [5], is a powerful tool with which to study these systems.

During the early years after the discovery of SERS it was puzzling that no observation of SERS due to adsorbed H_2O was reported even though aqueous electrochemical systems were actively investigated. Eventually, it was discovered that in very concentrated solutions ($\geq$1M) of Cs, Rb, or K halides, SERS of adsorbed H_2O and D_2O was readily observed presumably because the hydrogen bonded structure of water was disrupted. Subsequently, extensive studies of the effects of electrolytes, types of electrodes, temperature and pH range on the SERS of H_2O have been reported [6-12].

Recently [13], we reported that the spectra due to interfacial H_2O were observed with SERS from Ag electrodes in very dilute solutions of alkali halides ($\sim 10^{-3}$M), including NaCl and LiCl, which also contain 10^{-5}M $KMnO_4$. The role of the Mn species is not clear, but the spectrum of the adsorbed H_2O is identical to that obtained in concentrated alkali halide solutions. This implies that H_2O is bound to the Ag surface with the manganese playing the role of an organizer of the layers of H_2O in the interfacial region. This effect has been seen in other systems using the technique of ESDIAD where, for instance, the ability of less than a monolayer of adsorbed Br to order a subsequent addition of H_2O on

a Ag(110) surface has been observed[14,15].

For solutions with high interfacial pH, SERS is observed for adsorbates identified as OH^- or OD^- in addition to H_2O/D_2O in concentrated KCl electrolytes [16]. If alkaline earth halides or Li^+ and Na^+ halides are used instead of KCl, two peaks identified as OH^- are observed in the stretching region. It was postulated that the OH^- ion orients in two ways with respect to the surface normal: the oxygen is bonded to the Ag surface (3680 cm^{-1}) or the oxygen is attracted to the alkaline earth ions in the Helmholz layer with the hydrogen end pointing towards the Ag surface (3595 cm^{-1}). The major evidence for the assignment of the peaks to OH^- is:

1) the spectral peaks are observed if the bulk solution pH is high ($\sim$11).

2) the peaks disappear upon the addition of HCl (pH = $\sim$2).

3) prolonged electrolysis at -1.7 V_{SCE} (saturated calomel electrode reference) producing H_2 increases the interfacial OH^- concentration which is then detected with SERS.

4) isotopic substitution of OD^- for OH^- is in accord with expectation, and

5) the SERS peaks are observed at energy shifts similar to but somewhat higher than those found for OH^- (OD^-) in alkali halide single crystals.

An important consequence of these studies is that the supporting electrolyte does not play a benign role in the determination of the adsorbed water-like species. In particular, the cationic species determines whether the surface is predominately covered by water or hydroxide. The more important implication is that corrosion processes in dilute aqueous media proceed by numerous pathways depending on the concentration and composition of dissolved salts which affect the interfacial water structure..

In this paper we report the observation of the SERS spectra due to OH^- species on a Ag electrode in dilute aqueous $MgCl_2$ electrolytes (10^{-2} - 10^{-3}M) in the presence of 50

μM $KMnO_4$ or Cl_2. The hydroxide species, identical to those observed with concentrated alkaline earth halide solutions without the oxidizer, demonstrate that the adsorbates are attached directly to the Ag surface. Furthermore, the chemical equivalence of $KMnO_4$ and Cl_2 in inducing hydroxyl adsorbates points to a mechanism in which the surface charge of Ag is modified such as to induce the formation of organized water type adsorbates in the presence of Mg^{+2}.

EXPERIMENTAL

The SERS spectra were measured using an Ar^+ laser operating at λ=514.5nm at an incident power of 100mW focused on $\sim$1mm^2 surface area of the Ag electrode. The image of this illuminated spot was focused on the entrance slit of the triple stage spectrograph and the dispersed light was measured with an optical multichannel linear diode array detector. The data collection and messaging were performed with a minicomputer.

The polycrystalline Ag working electrode, along with a saturated calomel cell (SCE) and a platinum counter electrode was immersed in the electrolytic solution in a fused quartz optical cell. The counter electrode was placed behind the Ag electrode which was covered with epoxy except for the laser exposed surface. Standard methods of voltammetry were used to oxidize and reduce Ag to reform the electrode surface. Typically, the working electrode voltage relative to the saturated calomel cell (V_{SCE}) was ramped at 5mV/s.

Distilled water and reagent grade chemicals were used, and the pH of the electrolyte, monitored continuously , did not change significantly during a run. The solutions were purged of oxygen by bubbling N_2 gas into the electrolyte for several minutes prior to a ORC.

RESULTS

$KMnO_4$/MgCl$_2$. The SERS spectrum obtained from a Ag electrode after a second ORC in a 0.01M $MgCl_2$ solution containing 50μM $KMnO_4$ at a pH=9.62 is shown in Fig. 1a,b. Figure 1a depicts the frequency shift region near the O$-$H stretching region at

~3600^{-1} and Fig. 1b shows the low frequency region for a similar ORC. The sequence of V_{SCE} for the second ORC is as follows: After the initial ORC, V_{SCE} is swept to +0.1V and then switched to sweep cathodically (negatively with respect to SCE). When V_{SCE} is linearly ramped to -1.59V_{SCE}, appreciable H_2 forms at the cathode as evident from the increase in the reduction current shown at the right in Fig. 1. The initial peak at 3677 cm^{-1} (peak A) vanishes during the ORC during which Faradaic current flows. Immediately after the reduction is complete at 0.04 V_{SCE}, the peak reappears with an unresolved shoulder at 3660 cm^{-1}. As V_{SCE} is swept cathodically a small but perceptable shift of peak A towards lower Raman frequency shift is observed. At $-0.33V_{SCE}$, *three* peaks form which, at $-1.69V_{SCE}$, occur at 3684 cm^{-1} (peak C), 3648 cm^{-1} (peak D) and 3584 cm^{-1} (peak E). This spectrum is nearly identical to that previously reported for the formation of OH$^-$ adsorbates on Ag electrodes [11]. However, only peaks C and E were observed, a fact which formed the basis for the model in which the OH$^-$ was oriented either with the oxygen at the Ag surface or pointed with the oxygen toward the double layer. The observation of three peaks argues against this model.

In the low frequency shift region, two peaks (F and G respectively in Fig. 1b.) are evident at 533 and 458 cm^{-1} prior to the Faradaic portion of the ORC. These peaks occur at energy shifts reminencent of those found for the Ag$-$O stretching mode of adsorbed OH$^-$ and H_2O (500 and 415 cm^{-1}) [13], and for the metal oxide vibrations of cathodically deposited Ni(OH)$_2$ on a roughened Au surface[17]. After the Faradaic current ceases, peak G is still evident along with a new peak at 795 cm^{-1}, peak H. During the cathodic sweep, peak F again grows in intensity originating roughly with the onset of H_2 production at $-1.14V_{SCE}$. However, it is accompanied by several broad, unresolved, high-frequency components. On the other hand, peak G has nearly a constant intensity with a small maximum at $-0.67V_{SCE}$ coinciding with an increase in peak I at 1610 cm-1 which is due to the bending mode of adsorbed H_2O.

Peak H, formed immediately after the Faradaic reduction, decreases to zero intensity

at the onset of H_2 evolution implying that it is not an adsorbed OH^- species. Switching to an anodic sweep at $-1.59V_{SCE}$, the processes are found to be reversible with the exception that peak H does not reappear.

$Cl_2/MgCl_2$. Figure 2a,b show the SERS spectra obtained under conditions similar to those just described except that the electrolytic solution (pH=10.2, 0.01M $MgCl_2$) contains 50 μM Cl_2 rather than $KMnO_4$. Comparison of Figs. 1 and 2 show that nearly the same results are obtained regardless of the oxidizer. Yet without the oxidizer, no SERS spectra are obtained with this concentration of $MgCl_2$ or less. In other experiments in which alkali halides were used with Cl_2, no SERS spectra were obtained under similar conditions. This indicates that a common surface structure of adsorbed OH^- is formed at the Ag electrode interface regardless of oxidizer and it is like that obtained in concentrated $MgCl_2$ without oxidizer.

Similar spectra are obtained using electrolytes with a pH as low as 3.5, implying that the adsorbates are not simple hydroxides. Unlike the case of alkali halides with $KMnO_4$ as the oxidizer,[13b] the addition of O_2 at 1 atm does not change the spectra regardless of V_{SCE}. It should also be noted that 0.01M $MgBr_2$ solutions with or without Br_2 at $\lambda_{ex} =$ 488.0nm produced strong identical spectra.

Estimates of the relative surface concentrations of metal impurities were made secondary ion mass spectrometry. Similar electrodes and ORC conditions were used to remove and redeposit $\sim$ 20 atomic layers of Ag in solutions of $MgCl_2$ with $KMnO_4$. The surface concentration of Mg was found to be five times that of Mn at a depth of 10nm where the Mn/Ag mole ratio was 1/400. It is assumed therefore that a fresh Ag electrode surface after an ORC is contaminated with $\sim$1% Mn or Mg or less. Yet it is obvious that they have a major influence on the nature of the adsorbates as observed with SERS.

DISCUSSION

Recently, there have been several detailed reports on the ability of impurity atoms on

metal surfaces in a high vacuum environment to induce an ordered surface structure of adsorbate molecules such as H_2O on Ag(110). As noted before an example is the ESDIAD study of a Ag(110) surface which is exposed to less than a monolayer of Br_2 before exposure to H_2O vapor. In the absence of adsorbed Br, adsorbed H_2O forms a disordered ice structure, but the pretreatment with Br causes an ordered hydrogen bonded polymer to form.[15]

In other experiments preadsorption of less than a monolayer of O_2 rather than Br on Ag(110) followed by exposure to H_2O forms an ordered array of OH.[18]. Additional exposure to H_2O causes the formation of a hydrogen bonded array of H_2O and OH^- which is reminescent of the hydrogen bonded structure of $LiOH\cdot H_2O$.[19]

Recent molecular dynamics calculations have demonstrated the ability of a Cl^- ion, for example, to order clusters of H_2O in conformations not usually expected. For instance $Cl^-(H_2O)_4$ has a hydrogen bonded structure in which the Cl^- is at the apex of a square pyramid whose base is formed by the four oxygens of the H_2O molecules.[20]

While none of these systems is directly applicable to the solution interface of a Ag electrode in a $MgCl_2$ electrolyte, they do point to the need to consider rather uncommon surface adsorbate structures. In the early work on the the SERS of H_2O, concentrated alkali halides were used because it was felt that the hydrogen bonded H_2O structure was disrupted by the high concentration of hydrated ions. With the discovery that adsorbed H_2O is easily observed in very dilute alkali halide electrolytes, it may be surmised that a small surface mole fraction of adsorbed M^+ or M^{+2}, where M is a group IA or IIA metal, increases the interfacial structural order of adsorbed H_2O species by changing the surface charge distribution. From the data of our SERS spectra alone, it is not possible to arrive at an unabiguous surface structure. However, it is possible to make some plausible arguments that the surface has both adsorbed H_2O and OH^-.

The common growth of peaks E and F as the H_2 discharge current increases is an argument for the formation of OH^-. Previously, peak E was assigned to OH^- in which

the oxygen is attracted to Mg^{+2} cations in the outer Helmholz plane.[16] A less energically favorable orientation, as evidenced by the difference in hydration energies, is that where the oxygen end is bonded to the Ag surface. That we observe three peaks in the O-H stretching mode region and that we can observe the same spectra when the solution bulk pH is as low as 3.5 argues agains this interpretation.

An alternative model results if it is assumed that the surface structure of H_2O or OH^- is similar to that observed at an UHV interface which has been sequentially exposed to O_2 and H_2O.[18] In our case since the Ag surface is reconstructed during an ORC in an aqueous medium, it is largely covered by disordered hydrogen-bonded H_2O molecules. Furthermore, Mg^{+2} ions are adsorbed onto this surface replacing Ag atoms to form a dilute distribution of impurity sites with high positive charge. It is expected that OH^- ions are strongly bonded to these Mg^{+2} sites as a comparison of the bulk solution stability constants of $MgOH^+$ and AgOH suggests.[21] In addition Ag atom size restrictions limit the number of site geometries available for OH^- to two which we will label I and II. The role of the oxidizing agent, as previously discussed[13] is to provide a constant reformation of the surface due to the diffusion controlled oxidation. This process is evidenced by the small reduction current observed regardless of V_{SCE}.

Site I occurs at the outermost surface layers of the (100), (110), or the (111) planes when a Mg^{+2} replaces a Ag. OH^- ions are readily adsorbed to provide SERS active centers sensitive to voltage tuning of the vibrational frequency since they protrude into the Helmholz field. In the case of the (100) or (111) planes, Mg^{+2} ions, incorporated into the second layer of the lattice, are shielded electrostatically by neighboring Ag atoms to reduce the electric field experienced by an OH^- ion. More importantly, geometry restrictions prevent OH^- ions from occupying surface interstitial sites ($r_{OH} = 1.4A$, $r_{100} = 0.6A$ for the octahedral intersitital site of Ag metal) which are the only possible sites for interaction with second layer Mg^{+2}. Consequently, only Type I sites exist on the (100) or (111) surfaces.

The situation for the (110) surface is different. Figure 3 shows that there are two sites for the adsorption of OH^-: one on the ridge which is a Type I site again, and the other, Type II, is in the trough which is parallel to the (110) direction. Presumeably OH^- adsorbates in the trough are not normal to the surface; conforming to the results obtained under UHV conditions.[18] These sites are further influenced if OH^- or H_2O moieties are adsorbed on the adjacent ridge lattice points as shown and labeled IIa and IIb respectively in Fig. 3. Hydrogen bonding of these species with the OH^- in the trough will vary causing different frequency shifts. The IR spectra of LiOH and $LiOH \cdot H_2O$ serve as models to predict the relative frequency shifts for sites IIa and IIb.[19] In LiOH, hydrogen bonding is considerably less than that which occurs between OH^- and H_2O in $LiOH \cdot H_2O$. The Raman frequency shift is therefore greater in LiOH. If an OH^- is on a ridge, then hydrogen bonding is minimized as in LiOH. The SERS spectra for the OH^- stretching mode is expected to be at larger shift than for the case where H_2O molecules on the ridge are hydrogen bonded to an OH^- in the trough (Type 2b). This case is much more like that for $LiOH \cdot H_2O$.

Based on this analogy when H_2 is evolved on the Ag cathode, OH^- is adsorbed on Type I sites and the SERS peaks E and F of Fig. 1 can be assigned to $MgO-H$ and $Mg-OH$ stretching modes. Peak C is assigned to the $O-H$ stretching mode of a Type IIa site and peak D is the corresponding mode at a Type IIb site. That there is H_2O on the surface is evidenced by peak G which has been previously identified as the stretching mode of $Ag-OH_2$.[13]

If V_{SCE} is swept anodically after H_2 production has occurred as in Fig. 1, the predominant species adsorbed on the surface will be OH^- at Type I sites as evident by peak A. After a second ORC both Type I and II OH^- adsorbates are formed due to the rapid Ag^+ reduction processes as shown by the appearance of peak B as well as peak A and a broadened peak F. During the cathodic sweep of V_{SCE}, some of the OH^- is protonated to form adsorbed H_2O as indicated by the increase in intensity of peak G, and the decrease of peak A and B before the onset of H_2 production at $\sim -0.8 V_{SCE}$. At V_{SCE} more negative

than this, Type I sites are increasingly more predominant because of the rapid production of H_2 and adsorbed OH^-.

If a fast cathodic sweep is used (25 mV/s), peak C is more intense relative to peak E shortly after -0.9 V_{SCE} than with a slow sweep (5 mV/s), but becomes less intense at more negative voltages. Peak E, however, grows in intensity even after switching to an anodic sweep. Thus, the dynamic processes of H_2 production favor Type I sites over those of Type IIa. This kinetic effect is expected if, during the cathodic sweep, the outer surface layers become increasingly covered with adsorbed Mg^{+2} due to electrostatic attraction to the cathode. In contrast, the number of Type II sites will remain essentially unchanged in this process.

CONCLUSIONS

It has been shown that micromolar quantities of the oxidizing agents $KMnO_4$, Cl_2, and Br_2 in the presence of $10^{-3}M$ Mg^{+2} activate a Ag electrode surface forming an adsorbed layer of OH^- ions which is very similar to that previously observed in concentrated electrolytes only. Three distinct surface sites are formed during the continuous diffusion controlled oxidation: Type I, a Mg^{+2} adsorbed in the outermost Ag surface layers; Type IIa, a Mg^{+2} ion in the trough of the (110) surface with a OH^- on the ridge; Type IIb, a Mg^{+2} ion in the trough with a H_2O molecule adsorbed on the ridge. In each site, the Mg^{+2} site polarizes the Ag surface to tightly bind OH^-. While this model is not unique, it is in conformity with the results recently obtained for adsorbed OH^- and H_2O at the vacuum metal interface and previous SERS results for dilute electrolytic solutions. The implication of these results is that small surface concentrations of metal ion impurities on Ag surfaces strongly influence whether O^{-2}, OH^-, or H_2O is the principal adsorbate.

Acknowledgements

References

1. J. D. E. McIntyre and W. F. Peck, Jr in *The Chemistry and Physics of Electrocatalysis*, J. L. McIntyre, M.J. Weaver, and E. B. Yeager, eds., Proc. Electrochem. Soc. PV 84-12 (1984) p102

2. E. M. Stuve R. J. Madix, B. A. Sexton, Surface Sci. **111**, 11 (1981)

3. C. Yang and W. E. O'Grady, J. Vac. Technol. **20**, 925 (1982)

4. C. J. Sandroff, S. Garoff and K. P. Leung, Chem. Phys. Letters **96**, 547 (1983)

5. M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985)

6. M. Fleishmann, P. J. Hendra, I. R. Hill and M. E. Pemble J. Electroanal. Chem. **117**, 243 (1981)

7. B. Pettinger, M. R. Philpott, and J. G. Gordon, II, J. Chem. Phys. **74**, 934 (1981)

8. B. Pettinger and L. Moerl, J. Electroanal. Chem. **150**, 415 (1983)

9. M. Fleishmann and I. R. Hill, in *Surface Enhanced Raman Scattering*, eds. R. K. Chang and T. E. Furtak. Plenum Press, NY, (1982)

10. S. H. Macomber and T. E. Furtak, Surface Sci. **122**, 556 (1982)

11. T. T. Chen, J. F. Owen, R. K. Chang, and B. F. Laube, Chem. Phys. Letters **89**, 356 (1982)

12. B. Pettinger, M. R. Philpott, J. G. Gordon II, Surface Sci. **105**, 469 (1981)

13. P. B. Dorain, a) J. Phys. Chem. **90** 5808 (1986), b) J. Phys. Chem. **90** 5812 (1986)

14. T. E. Madey, Science **234**, 316 (1986)

15. K. Bange, T. E. Madey, J. K. Sass, **162**, 252 (1985)

16. T. T. Chen, R. K. Chang, B. L. Laube, Chem. Phys. Letters **108**, 39 (1984)

17. J. Desilvestro, D. A. Corrigan, M. J. Weaver, J. Phys. Chem. **90**, 6408 (1986)

18. K. Bange, T. E. Madey, J. K. Sass, E. M. Stuve, Surface Sci. **183**, 334 (1987)

19. L. H. Jones, J. Chem. Phys. **22**, 22 (1954)

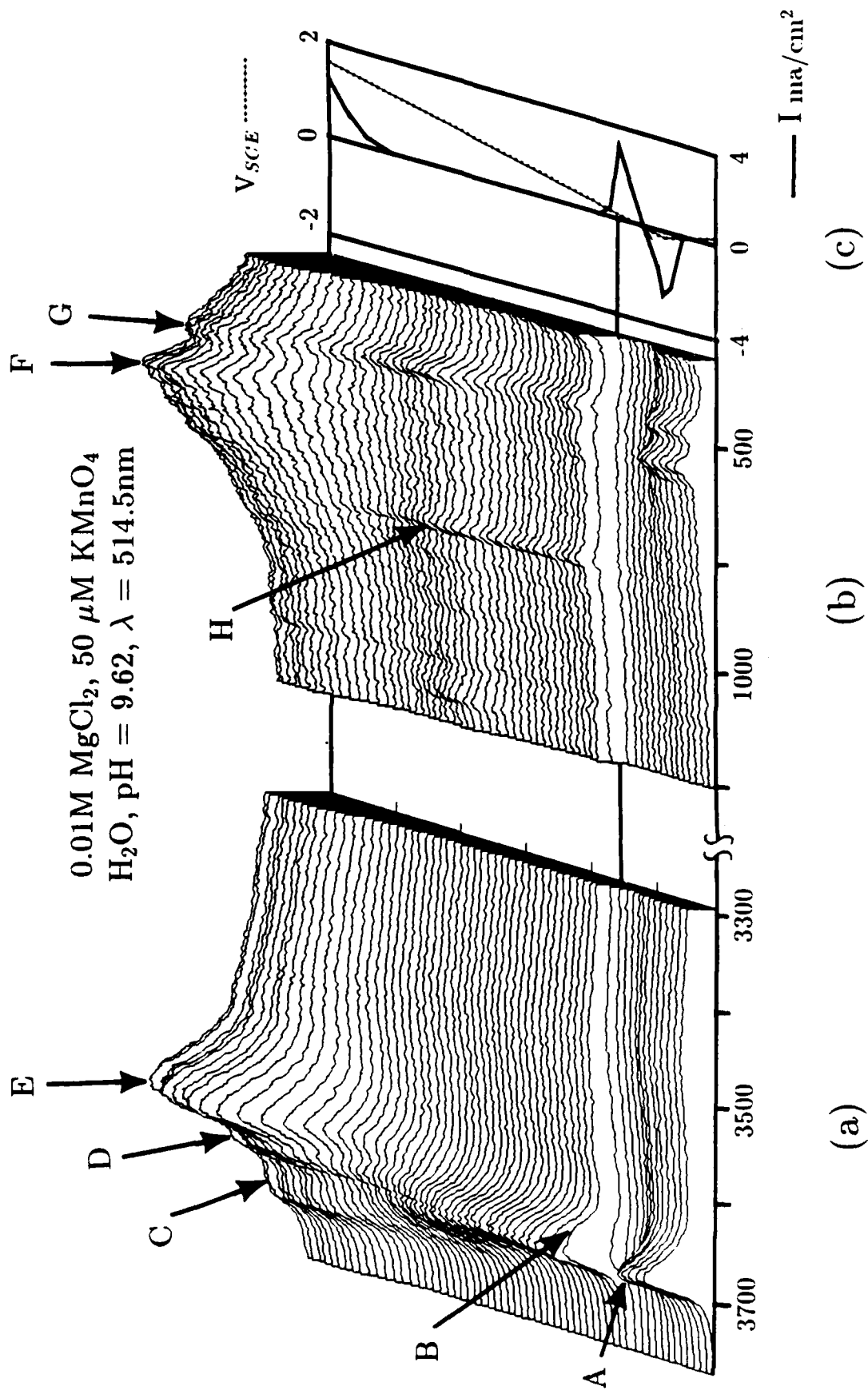20. S. S. Sung, P. C. Jordan, J. Chem. Phys. **85**, 4045 (1986)

21 *Critical Stability Constants*, R. M. Smith and A. E. Martell, eds., Plenum Press (New York, 1977)
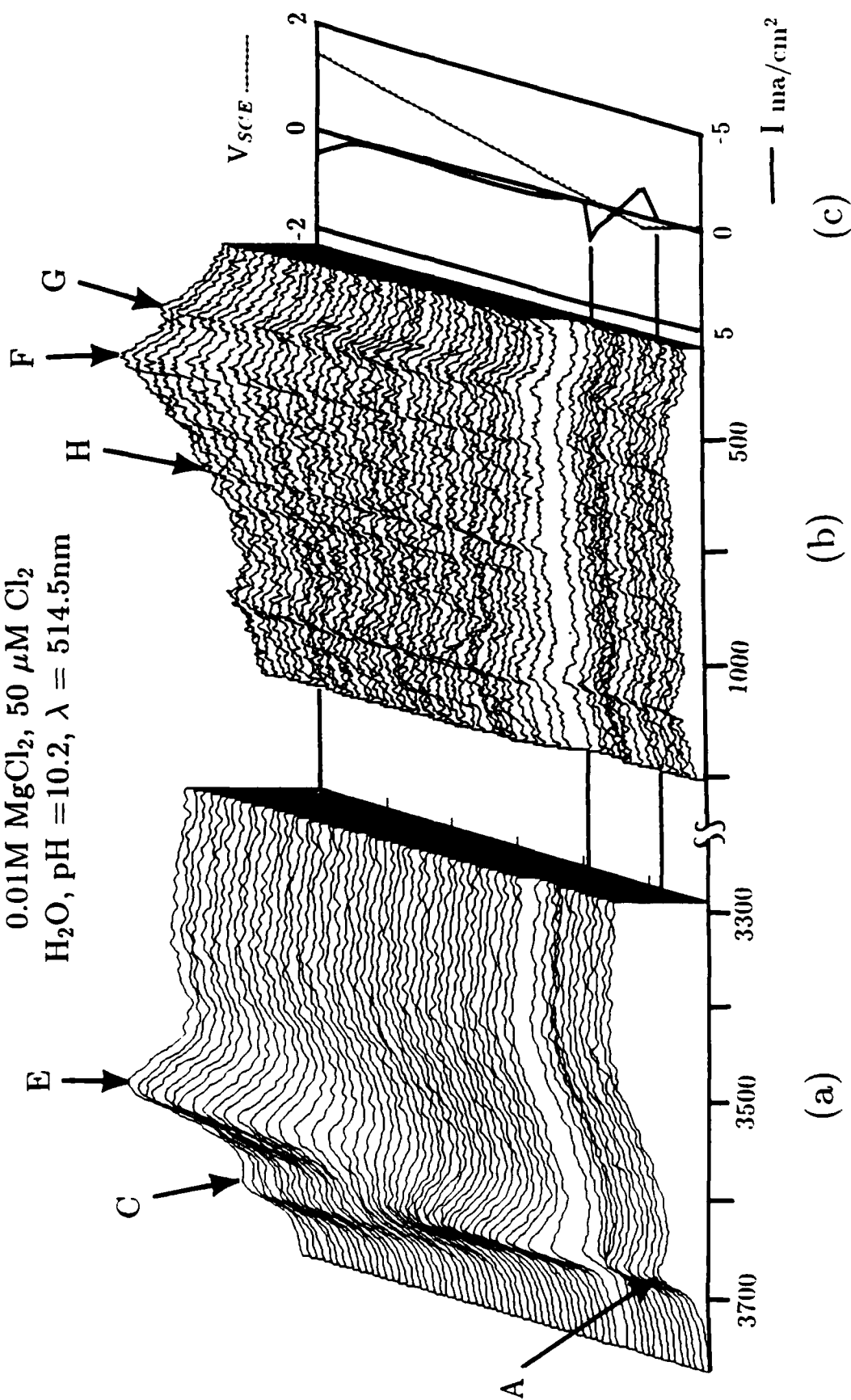
Figure Captions

Fig. 1. The SERS spectra obtained from a Ag electrode immersed in 10^{-2}M MgCl$_2$, pH = 9.62 and 50μM KMnO$_4$ solution a a function of V$_{SCE}$. a) The O$-$H spectral region. b) The low frequency modes for the M$-$OH region and c) the voltammogram which is presented in an 'unfolded' style. Spectra a) and b) were obtained in two separate but nearly identical experiments.

Fig. 2. The SERS spectra obtained from 10^{-2}M MgCl$_2$, pH=10.2, 50μM Cl$_2$ solution as a function of V$_{SCE}$. The conditions were similar to those of Fig. 1. Note that the current density scale in c) is reversed from that in Fig. 1.
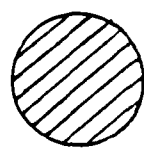
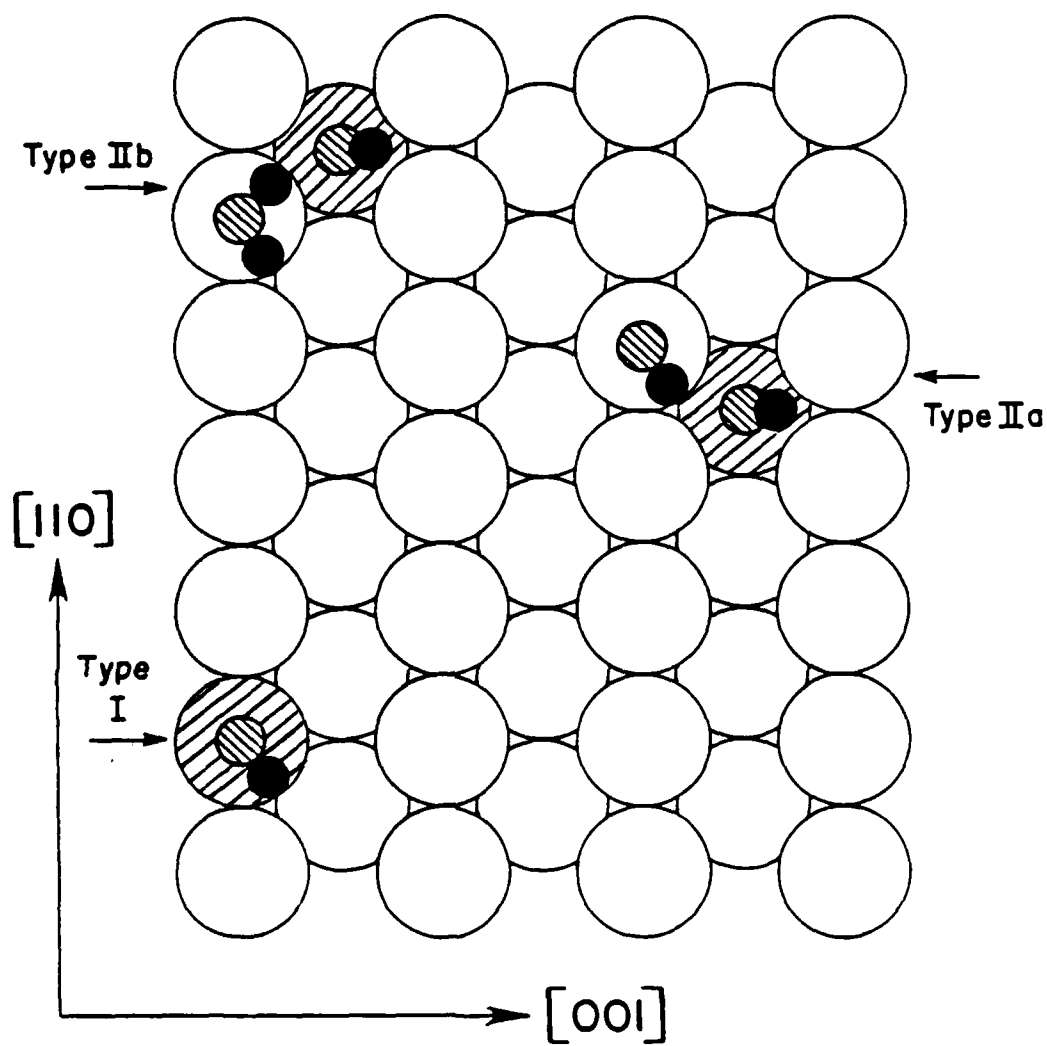Fig. 3. A schematic of a (110) Ag surface showing the Type I and Type IIa,b sites. It is assumed that a Mg^{+2} impurity ion is incorporated at the site during an ORC or in subsequent surface reconstruction by the oxidizing agent. The random H$_2$O water structure on much of the Ag surface has been omitted for clarity of presentation.

0.01M MgCl$_2$, 50 μM KMnO$_4$
H$_2$O, pH = 9.62, λ = 514.5nm

V$_{SCE}$ ·······

I na/cm^2

RAMAN SHIFT, cm^{-1}

(a)

(b)

(c)

0.01M MgCl$_2$, 50 μM Cl$_2$
H$_2$O, pH =10.2, λ = 514.5nm

V$_{SCE}$ ------

— I ma/cm^2

(a)   (b)   (c)

RAMAN SHIFT, cm^{-1}

Type IIb

Type IIa

[110]

Type
I

[001]

Mg^{+2} OH^-

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

9-87

DTIC